REMARKS

Paragraph 2 of page 6 of the originally filed specification and Claims 5 and 19 have been amended to correct a typographical/editorial error relating to the designation of "R5". The correct designation of R5 is set forth in U.S. Patent No. 5,529,125 (see, for instance, col. 3, 1, 5 of U.S. Patent No. 5,529,125), incorporated by reference in the second paragraph of Applicants' originally filed specification. Claims 1, 2, 16 and 20-23 have been amended to correct editorial errors in terminology. Entry of this amendment is therefore respectfully requested.

Respectfully submitted,

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Where R1, R2 and R3 may be hydrogen, alkyl, aryl, phosphonates, phosphates, acyl, amine, hydroxy and carboxyl groups, and R4 and R5 may consist of hydrogen, sodium, potassium, ammonium or an organic radical. Examples of 10 these materials include aminotri (methylene phosphonic acid) and its pentasodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid and its tetrasodium salt, hexamethylene-diaminetetra (methylene phosphonic acid) and its hexapotassium salt, and diethylenetriaminepenta (methylene phosphonic acid) and its hexasodium salt.

Among the phosphonate materials evaluated, emphasis was concentrated on aminotri (methylene phosphonic acid), herein referred to as "HZ acid," available in 50% strength as "DEQUEST 2000" from Monsanto Co.; 1-hydroxyethylidene-1,1-diphosphonic acid, herein referred to as "HV acid," available in 60% strength as "DEQUEST 2010" from Monsanto Co.; and diethylene triamine penta (methylene phosphonic acid), herein referred to as "HY acid," available in 50% strength as "DEQUEST 2060" from Monsanto Co. Table 1 shows the inhibition of calcium and magnesium silicate scale buildup using these different phosphonate compounds and mixtures thereof.

TABLE 1

INHIBITOR 100 PPM	24 HOURS @ 50° C. INHIBITION		
HZ Acid	N/A		
HV Acid	22		
HY Acid	12.2		
HV + HY (1:1)	14.2		

The phosphonate materials were also evaluated because of their potential for retarding the acid reaction with clays and their ability to slowly hydrolyze ammonium bifluoride or ammonium fluoride to produce hydrofluoric acid. By titrating various phosphonate acids with tetra methyl ammonium chloride, the acidity constants of the different acids was determined. These are set forth in Table 2.

TABLE 2

ACID	N° ACIDITY CONSTANTS	pK,	pK ₂	pK ₃	pK₄	pK,
HY	10	<2.0	<2.0	<2.8	4.5	<5.5
HZ	6	<2.0	<2.0	<4.3	<5.4	<6.7
HV	5	<1.0	<2.5	<7.0	<11.4	_

It is known that under downhole conditions, the acid's pH remains between 1 and 3. This implies that not all of the 55 hydrogen ions (H*) are used so that their utilization is dependent on the spending of the solution. From Table 2, it can be seen that the HY acid should produce the slowest hydrolysis rate. These materials are hydrolytically and thermally stable, with some materials being stable up to temperatures as high 400° F.

Overall, the HY, HV, and HZ acids are weak acids, however when evaluated for the first and second hydrogen (i.e. pK₁ pK₂) they behave as moderately strong acids. Table 3 shows a comparison of the phosphonate acids used to 65 standard mineral and organic acids used in oil field related treatments.

TABLE 3

ACID	_p K ₁ (STRONGEST HYDROGEN)		
HYDROCHLORIC ACID	<1		
HV ACID	<1		
HY ACID	<2		
CITRIC ACID	<3.1		
HYDROFLUORIC ACID	<3.5		
FORMIC ACID	<3.8		
ACETIC ACID	<4.8		
BORIC ACID	<8.7		

A pK value below 2 is regarded as a strong acid, while a pK value between 2 and 3 is regarded as a moderately strong acid, a pK value of between 4 and 7 is a weak acid, and a pK value above 7 is characterized as a very weak acid.

In order to evaluate the effect of phosphonates on the solubility of quartz and clays, several mixtures of the phosphonate acids were prepared using ammonium bifluoride as the source of hydrofluoric acid. The phosphonate acid mixtures were then tested along with standard hydrofluoric acid systems and other commercially available retarded acid systems using static and dynamic solubility tests. The commercially available retarded acid systems used consisted of "CLAY ACID", "RMS ACID" and "RHF ACID". "CLAY ACID" is a fluoroboric acid solution available from Dowell Schlumberger. "RMS ACID" is available from BJ Services and consists primarily of a hydrochloric acid and hexafluorophosphoric acid mixture. The "RHF ACID" is a retarded hydrofluoric acid system consisting of 12% hydrochloric acid and 3% hydrofluoric acid using ammonium bifluoride as the source of hydrofluoric acid and an aluminum salt as a retarder. "RHF ACID" is available from Halliburton Company.

To simulate quartz, 20-40 mesh sand was used instead of formation quartz, and bentonite and kaolin clay were used to simulate formation clays. Tests were also conducted using a mixture of sand and clay in an 80:20 ratio to simulate a typical sandstone formation. All the solubility tests were performed at 180° F. which appeared to be the critical temperature to effectively retard acid reaction rate with clays. For FIGS. 1-3, the concentration of the HY acid was 3% by volume of the total solution (4.1% by weight). For HV acid the concentration was 3% by volume (3.0% by weight). For HZ acid the concentration was 3% by volume (3.1% by weight). The results of these solubility tests are presented in FIGS. 1-3. The initial reaction rates with quartz for the HY and HV acid, as shown in FIG. 1, are much higher than that of standard hydrofluoric acid. From FIG. 2, it can be seen that the phosphonate acids retard the reaction rate with clays during the initial 15 minutes. After this initial 15 minute period, the clay's solubility is limited as shown by the flattened portion of the curve of FIG. 2. FIG. 3 shows the same trends with a much lower solubility at all times for the three phosphonate acids used compared to the other acid systems.

Normally, during matrix acidizing of sandstone formations, extra hydrochloric acid is used to prepare the hydrofluoric acid solutions. Keeping the pH low during the treatment prevents precipitation of fluorides, i.e. Ca, Mg, etc. . . , and favors precipitation of the more soluble fluorosilicates. To determine how the phosphonate acid/hydrofluoric acid systems work using various concentrations of hydrochloric acid, tests were conducted to determine the reaction rate of these acids with quartz and clays. The results are presented in FIGS. 4 and 5. The concentration of the HY acid was 3% by volume of the total solution (3.8–4.1% by